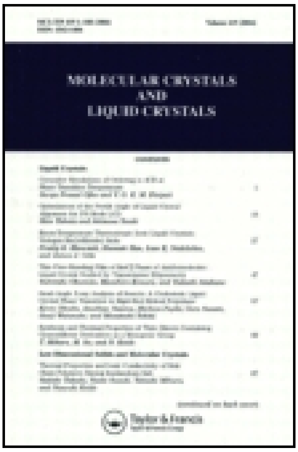

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New Application of Thermotropic Liquid Crystals

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New Application of Thermotropic Liquid Crystals

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Few liquid crystalline compounds and mixtures were tested as lubricating agents. The much decrease of friction coefficient was observed in comparison to the paraffin oil, the commonly used reference lubricant. The compounds were differing in chemical structure as well as the kind of formed liquid crystalline phases. The chemical structure plays a crucial role in the improvement of tribological properties.

Keywords Liquid crystals; lubricants

1. Introduction

The lubrication is the process contracting the inconvenient were of contacting metal surfaces. The mechanism of lubrication is based on the creation of adsorbed layer by a lubricating agent fulfilling irregularities of the surface. From the literature it is well known that lubricating agents such as graphite or carbon disulfide can be good lubricants because their ordered structure let to create the layers of easy gliding. In the literature it can be found that liquid crystals can be also used as lubricating agents [1–5]. Such compounds have polar groups which let the adsorption on the metal surface and formation of protecting ordered layers. The mechanism of action of these substances is still unknown. The aim of this work is to test different liquid crystalline compounds as lubricating agents to check the influence of chemical structure as well as the kind of liquid crystalline phases on the tribology properties.

2. Experimental Methods

The liquid crystalline compounds of the rod-like structure, shown in Table 1, were used for the investigation. The compounds have –NCS, –CN and –F terminal groups, additionally one compound has the Cl atom in the lateral position (compound ZCl). The used compounds and mixtures have liquid crystalline phases at room temperature. The nematic phase was for compounds 5CB, 6CB, 6CHBT,

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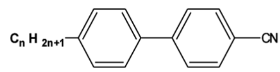
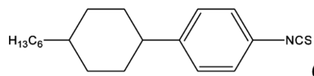
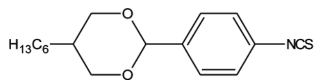
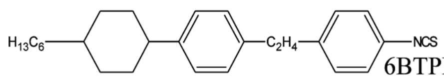
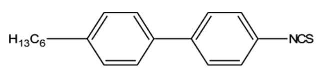
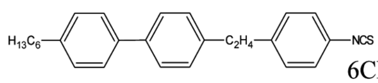
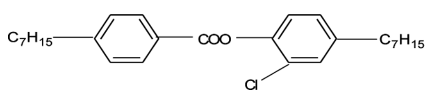
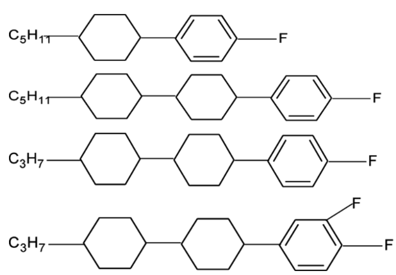
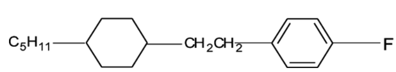
Table 1. Structure of investigated compounds and the composition of the mixtures used as lubricating agents as well as their acronyms

N	Acronyms and phase transition temperature	Structure
1	n = 5 (5CB): Cr 24.5°C N 35.3°C Iso	 nCB
2	n = 6 (6CB): Cr 14.5°C N 29°C Iso	
3	n = 8 (8CB): Cr 19.5°C S_{A1} 40°C Iso	
4	6CHBT: Cr 12.5°C N 43°C Iso	 6CHBT
5	Mixture S_{A1} Composition: 0,8 molar fraction of 6CHBT + 0,2 molar fraction of 6DBT Cr 23°C S_{A1}77°C Iso	 6DBT
6	Mixture S_B Composition: 0,8 molar fraction of 6CHBT + 0,2 molar fraction of 6BTPE Cr 23°C S_B 98°C N 116°C Iso	 6BTPE
7	Mixture S_E Composition: 0,8 molar fraction of 6CHBT + 0,2 molar fraction of 6BT Cr 22°C S_E55°C N 70°C Iso	 6BT
8	Mixture MN Composition: 0,8 molar fraction of 6CHBT + 0,2 molar fraction of 6CHBTPE Nematic in room temperature	 6CHBTPE
9	ZCl Nematic in room temperature	
10	Mixture MF Composition: the ratio of compounds 1:1:1:1 Nematic in room temperature	
11	Isotropic	

ZCl, mixture MN – composed of two compounds with –NCS group in terminal position and mixture MF – composed of four compounds with fluorine atom in terminal position. The monolayer smectic A_1 phase was for compounds 8CB and bicomponent mixture S_{A1}. The other bicomponent mixtures S_B and S_E have smectic B and E phases, respectively, additionally to nematic phase.

Friction coefficient values for substances were compared with the value for pure paraffin oil used as modeling lubricant substance as well as for isotropic compound.

The compounds were synthesized in Military University of Technology in Warsaw, The compounds and mixtures were measured with the use of T-11 tribotester, produced by ITME in Radom.

For tribological measurements the100Cr6 steel samples were used. Ball of the diameter equal to 0.5", roughness $R_a = 0.032\,\mu m$ and hardness 60–65 HRC was used as a sample. The disc of the diameter equal to 25 mm, surface roughness $R_a = 0.175\,\mu m$ and hardness 45 HRC was used as a counter-sample. The samples were made according to the requirements of tribotester T-11. Measurements were performed at ambient temperature. The value of friction force was measured and the friction coefficient was determined.

The measurements were carried on under the following conditions: applied load 20, 30, 40, 50 N, rubbing speed 0.1 m/s and test time 900 s. The measurements of friction force were performed continuously with frequency 1 s, directly with the use of tensometric sensor. The value of the friction coefficient was calculated dividing the value of the friction force, rescaled by operating program by the value of the load used.

The degree of wear was determined on the base of scars diameters on the ball surface (sample). The scars were measured in the direction parallel to the direction of friction by reflecting optical microscope Polar PZO. Moreover, the degree of wear was determined for some samples as the dimension of scars of steel counter-samples by scanning electron microscope SEM Hitachi S-3500 N.

3. Results and Discussion

For all tested lubricating substances the values of friction coefficient were stabilized after few seconds and have rested on the set level during the whole measurement. This is why, the friction coefficient was calculated as the mean value from 900 measurements. The mean values of friction coefficients are shown in Figure 1. For comparison, the results for paraffin oil, the commonly used testing lubricating agent, as well as for a compound of similar rod like structure but not forming liquid crystalline phase are presented. It was found that the friction coefficient for all tested liquid crystalline compounds and mixtures is lower than for paraffin oil. It proves the thesis that the liquid crystalline compounds can be used as good lubricating agent having properties better than commonly used paraffin oil.

It was found that the influence of the used load on the obtained results of friction coefficient is different for different tested materials. The coefficient increases and next decreases with the increase of the load, for example for 5CB, 6CB and 6CHBT, and the maximum is for 40 N, 30 N and 40 N, respectively. This behavior is the same as for paraffin oil, for which maximum value of friction coefficient is for the load 30 N. The opposite behavior, namely the decrease of the friction coefficient and next the increase with the load is observed for mixture S_E. The decrease is observed for compound 8CB and mixture S_{A1}, which form smectic A_1 phase, as

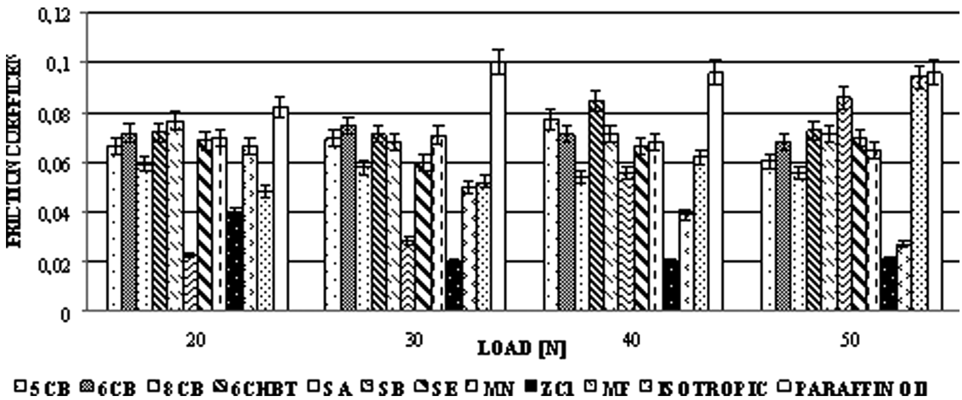


Figure 1. Friction coefficient of all tested lubricating agents for different load.

well as for compound ZCl and mixtures MN and MF, which form nematic phase. But the change is very small in the case of 8CB, S_{A1} and MN, being within an measuring error, and in the case of the mixture MN is large. The drastic increase of the friction coefficient is observed for the mixture S_B and compound existing only in an isotropic phase. These differences causes that it is difficult to say which factor is the most important. Probably both the chemical structure as well as the kind of formed phases play an important role.

Among liquid crystalline substances the lowest friction coefficient was obtained for compound ZCl having chlorine atom in the lateral position as well as for nematic mixture MF composed of compounds with fluorine atom in the terminal position. These results indicate that the existence of halogen atom in the molecular structure strongly influences the improvement of tribological properties. The use of the compound 6CHBT with the terminal group –NCS lower only a little bit the friction coefficient in the comparison to paraffin oil thus it has the lowest ability for reduction of the resistance of motion. The compounds with –NCS group are the components of mixtures exhibiting S_{A1}, S_B and S_E phases, what can be the reason that they also do not have good tribological properties.

The compounds with –CN terminal group: 5CB, 6CB and 8CB have higher ability for reduction of the resistance of motion than compounds with – NCS group. These three compounds belong to the same homologous series but shorter compounds 5CB and 6CB have nematic phase and longer 8CB has smectic A_1 phase. The last compound gives the best results, probably because of the difference in phase formation. The layered structure of the liquid crystalline phase could reduce friction coefficient. It is not always true, because for the mixture S_{A1}, which components have –NCS terminal group, these reduction of coefficient was not observed.

The length of wear scars on the surface of sample-ball, obtained after the friction process for all tested substances and mixtures, were studied by the optical reflectance microscope. The obtained results, presented in Table 2, show that the wear scars are not large and the influence of the used load is neglected. The lowest friction coefficient was observed for compounds 8CB and ZCl as well as for mixture MF. The length of wear scars, obtained during tribological test under the load 50 N with the use of 8CB, ZCl and MF, was also studied by scanning electron microscope SEM. The results are shown in Figure 2.

Table 2. Diameter of were scars of sample (ball) (S_s [mm]) after the use of different materials under the load F [N]

Compound	F [N]	S_s [mm]	F [N]	S_s [mm]	F [N]	S_s [mm]	F [N]	S_s [mm]
5CB	20	0,23	30	0,16	40	0,21	50	0,21
6CB		0,29		0,27		0,34		0,34
8CB		0,23		0,23		0,26		0,33
6CHBT		0,30		0,27		0,38		0,32
S_{A1}		0,28		0,28		0,34		0,34
S_B		0,30		0,43		0,34		0,36
S_E		0,25		0,31		0,30		0,34
MN		0,21		0,16		0,23		0,31
ZCl		0,38		0,31		0,20		0,37
MF		0,29		0,32		0,37		0,38
Paraffin oil		0,25		0,25		0,27		0,32

The diameter of wear scars is the smallest in the case of the use of 8CB as a lubricating agent and equals 350 μm. Next one is the mixture MF of compounds with fluorine atom (385 μm) and next the compound ZCl (475 μm). It corresponds to the sequence of changes of wear scars on the ball. But the changes are not large thus it can be conclude that the wear of the samples during the friction process is very small. The origin of such good tribological as well as antiwear properties of liquid crystalline materials can be the formation of easy glide layers.

To check the steel surface topography covered with liquid crystalline materials two apparatus were used: metallographic microscope with polarized light as well as atomic force microscope (AFM). The pictures obtained with their use are presented in Figures 3 (for all tested materials) and 4 (for mixtures S_{A1}, S_B, S_E), respectively. They show that liquid crystalline compound is sensitive to the roughness of the steel. This behavior is well known and it is used to orient liquid crystalline molecules in display cells. The presence of polar groups –CN, –NCS, –F and –Cl even increase the adhesion of compounds to the steel surface. During friction process the liquid crystalline molecules fill the microscars, forming easy glide layer.

For some compounds and mixtures which form nematic phase as well as different types of smectic phases the measurements of wetting process on the surface of

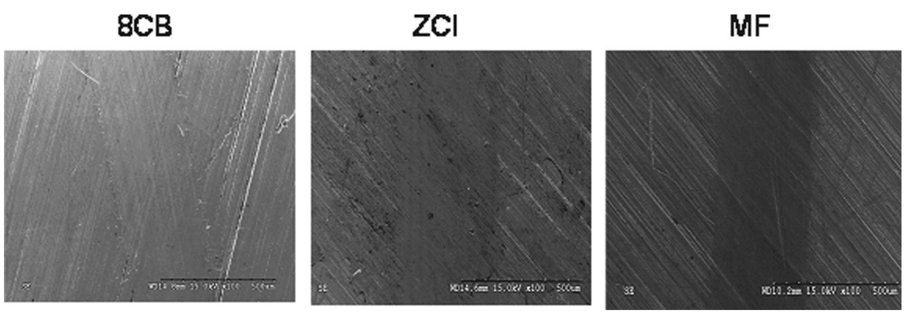


Figure 2. Pictures obtained by scanning electron microscope (SEM) of the were scars after friction process with the use of 8CB, ZCl and MF under load 50 N.

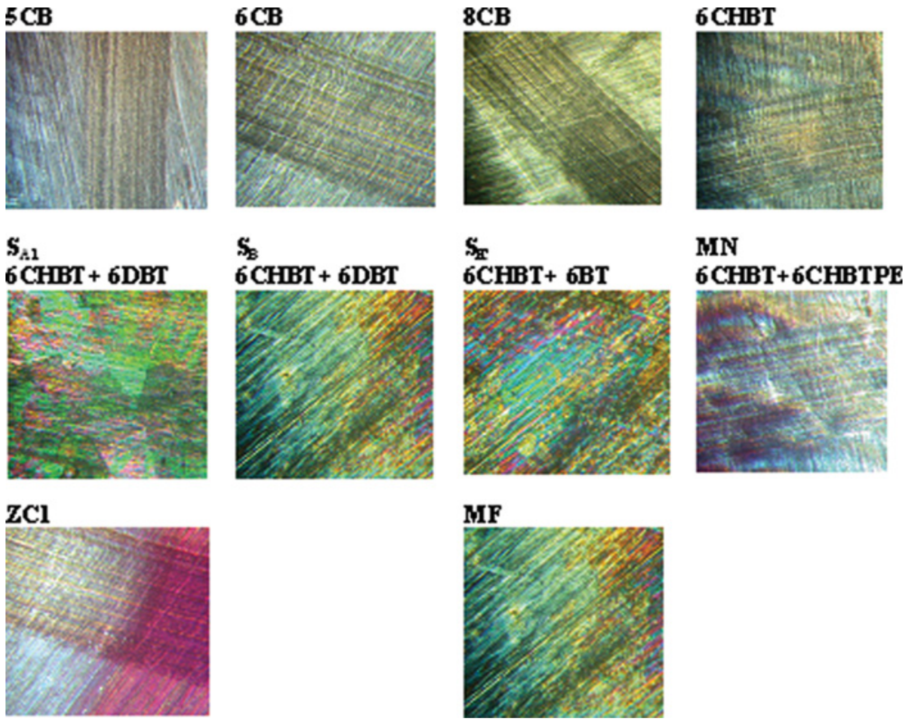


Figure 3. Pictures obtained by metallographic microscope of the surface covered with compounds having liquid crystalline phase. (Figure appears in color online.)

100Cr6 steel was tested. These measurements were carried on by the method of droplet geometry establishing. The results are presented in Figure 5.

The results of measurements have shown that tested compounds 5CB, 6CB and 6CHBT (in nematic phase) wet the steel surface very well because the wetting angles are not larger than 15°. It can be the reason of such good tribological properties of this compound. The good wetting of the 100Cr6 steel surface by the liquid crystalline materials is due to the chemical structure of compounds. The presence of polar terminal groups –CN and –NCS makes ease the adsorption of compounds on the steel surface.

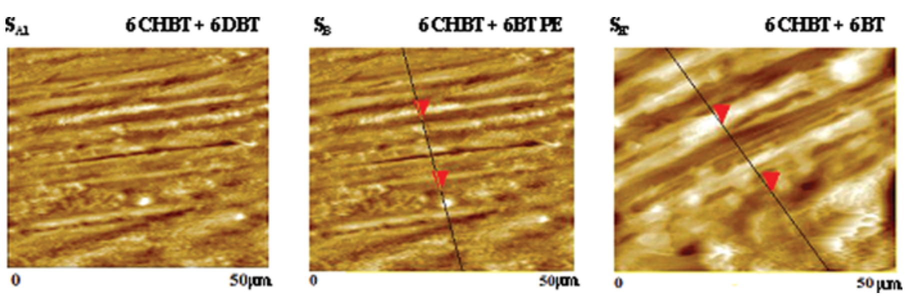


Figure 4. Pictures obtained by atomic force microscope (AFM) of the steel surface covered with mixtures having S_{A1}, S_B and S_E phases. (Figure appears in color online.)

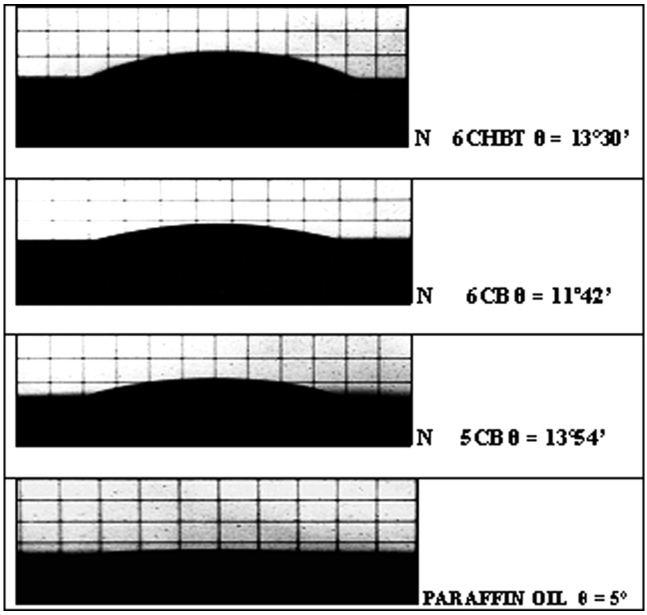


Figure 5. Wetting angle of steel surface by the liquid crystalline compounds and paraffin oil.

The biggest disadvantage of liquid crystalline materials used as lubricating agents is their big cost. The tribological tests of mixtures in which liquid crystalline compounds are used as an additive to a paraffin oil prove that even in the small concentration these compounds improve the tribological properties compare to pure paraffin oil [6].

4. Conclusions and Perspectives

The obtained results show that for all used liquid crystalline compounds and mixtures there is an increase of tribological properties in comparison to paraffin oil used as modeling lubricating agent. The following conclusions can be deduced:

1. The reduction of friction coefficient is bigger in the case of liquid crystals than paraffin oil.
2. The tribological properties of liquid crystalline substance depend on the kind of terminal group in the following way –F > –CN > –NCS.
3. The analysis of surface covered by termotropic liquid crystals with the use of AFM and metallographic microscope shows that the compounds concentrate in microscars of the surface.

Good triboligical properties of liquid crystals can be due to filling of microscars in surface and formation of easy glide layers minimizing energy during friction. The analysis of surface of counter-sample covered with liquid crystalline material under metallographic polarized microscope and atomic force microscope (AFM) confirm such explanation.

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